

Nitrilotriacetic Acid Degradation Under Microbial Fuel Cell Environment

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Abstract: The removal of nitrilotriacetic acid (NTA) was studied under anaerobic conditions using oligotrophic and copiotrophic microbial fuel cells (MFCs) as a novel wastewater treatment process. Over 85% of NTA was removed from oligotrophic MFCs enriched and maintained with fuel containing NTA, whilst the value was around 20% in oligotrophic MFCs fed with NTA-free fuel, and in copiotrophic MFCs enriched with NTA containing fuel. The oligotrophic MFCs generated current with concomitant utilization of NTA when served as the sole organic compound, suggesting that NTA is oxidized its suitability as fuel in the MFCs. © 2006 Wiley Periodicals, Inc.
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INTRODUCTION

Nitrilotriacetic acid (NTA) is a common industrial chelating agent and is used in laundry detergents as a builder to replace phosphates. NTA is an environmental concern owing to its contribution to the eutrophication of lakes and ponds (Bouveng and Davisson, 1972; Thomas, 2001) and its ability to solubilize and mobilize heavy metals from sediments and activated sludge (Kirk et al., 1981). NTA can be removed through the activated sludge process (Margarete and Thomas, 2001). An adaptation period of 1–4 weeks is required to achieve a maximum NTA elimination efficiency of 70%–90% in activated sludge plants (Margarete and Thomas, 2001). However, the elimination efficiency of NTA was found to be less than that of the overall organic load in the activated sludge process (Bouveng and Davisson, 1972) suggesting that NTA is not as readily degradable as the common organic contaminants.

A microbial fuel cell (MFC) has been proposed as a wastewater treatment mechanism (Jang et al., 2004; Liu et al., 2004; Min and Logan, 2004). MFCs have been used to enrich microbial consortia utilizing fuels including glucose, acetate, and lactate.

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This emerging technology is attractive since energy is recovered treating wastewater instead of consuming energy. Various chemicals used industrially and domestically end up in wastewater. MFC as a novel wastewater treatment process would be more attractive if this process can remove these organic contaminants including xenobiotics such as NTA. MFCs could remove general organic compounds including processing wastewater (Min and Logan, 2004). This article reports the removal of NTA in a mixture with common organic compounds and as sole carbon and energy sources.

MATERIALS AND METHODS

Copiotrophic and oligotrophic MFC systems were used to test NTA degradation efficiency under high overall organic load conditions and under poor nutritional conditions, respectively. The MFCs were enriched and maintained as described previously (Chang et al., 2004; Kang et al., 2003). Oligotrophic MFCs were enriched and maintained with artificial wastewater (AW) containing glucose and glutamate (10 mg/L as chemical oxygen demand (COD)) (Chang et al., 2004) or river sediment (Kang et al., 2003). In copiotrophic MFCs, AW was used with either 5 mM acetate (Lee et al., 2003) or glucose and glutamate (100 mg/L as COD) (Chang et al., 2004). NTA (Sigma Co., St. Louis, MO) was added to the AW to dissolve trace minerals at the final concentration of 10 mg/L, but not to the river water.

MFCs were operated in a continuous mode at a hydraulic retention time of 2.22 h based on the flow rate of 0.19 mL/min and a volume of 25 mL each in the anode and cathode compartment. The potential was measured using a multimeter (Keithley Instruments, Inc., Cleveland, OH) and recorded every 5 min to a personal computer through a data acquisition system (Testpoint, Capital Equipment Co., Richmond, VA). The potential was converted to current according to Ohm's law [current = potential/resistance]. NTA was quantified using a high-pressure liquid chromatograph (HPLC M720, Young-lin, Seoul, Korea) equipped with a UV detector (λ_{max} , 254 nm) and a symmetryTM C₁₈ column (Waters chromatography, Milford, MA) as reported by White

Table I. Removal of NTA in oligotrophic MFCs enriched with artificial wastewater containing glucose and glutamate (10 mg/L as COD).

Concentration of NTA (mg/L)		Removal efficiency (%)	COD removal efficiency (%)
Influent	Effluent		
21.8 ± 2.2	1.9 ± 0.2	91.3	83.5 ± 0.1
30.1 ± 0.6	3.1 ± 0.4	89.7	89.1 ± 0.1
48.5 ± 2.2	7.7 ± 0.9	85.2	88.9 ± 0.2

and Knowles (White and Knowles, 2000). COD was determined by the standard method (Greenberg and Eaton, 1995) using chromate as the oxidant. All experiments were repeated at least three times and the mean values are presented.

RESULTS AND DISCUSSION

Removal of NTA in MFCs

Oligotrophic MFCs enriched with AW containing glucose and glutamate were fed with the same fuel containing different NTA concentrations (Table I). Using an NTA concentration of 21.8 mg/L, 91.3% NTA was removed with a COD removal efficiency of 83.5%, while the NTA removal efficiencies were similar to those of COD with higher NTA concentration. These results show that NTA is utilized as efficiently as glucose and glutamate in oligotrophic MFCs.

A similar experiment was conducted using oligotrophic MFCs enriched with river water and copiotrophic MFCs enriched with glucose and glutamate (Table II). Less NTA was removed from these MFCs than with oligotrophic MFCs enriched with AW containing NTA. The oligotrophic MFCs enriched with river water showed an 18.5% NTA reduction with a COD removal of 62.0%. NTA comprises most of the remaining COD suggesting that NTA is not a good electron donor in MFCs enriched without NTA, while oligotrophic MFCs enriched with fuel containing NTA removed NTA efficiently. Thus, it is concluded that NTA can be used as an electron donor as efficiently as glucose and glutamate in oligotrophic MFCs enriched with NTA. Similarly, copiotrophic MFCs showed nearly complete removal of glucose/ glutamate or acetate, but the NTA removal efficiency was around 20%. From these results, the conclusion can be drawn that NTA is as easily degradable as the common organic contaminants in an oligotrophic MFC adapted to this

Table II. Removal of NTA in MFCs of different nutritional conditions.

MFC		Concentration of NTA (mg/L)			
		Influent	Effluent	Removal efficiency (%)	COD removal efficiency (%)
Oligotrophic	River water	19.3 ± 6.5	15.7 ± 7.4	18.5	62.0 ± 4.3
Copiotrophic	AW ^a	23.1 ± 0.2	19.2 ± 0.8	17.1	84.1 ± 1.8
	AW ^b	34.0 ± 1.2	27.1 ± 0.7	20.4	77.1 ± 0.1

^aGlucose and glutamate (100 mg/L as COD).

^bAcetate (5 mM).

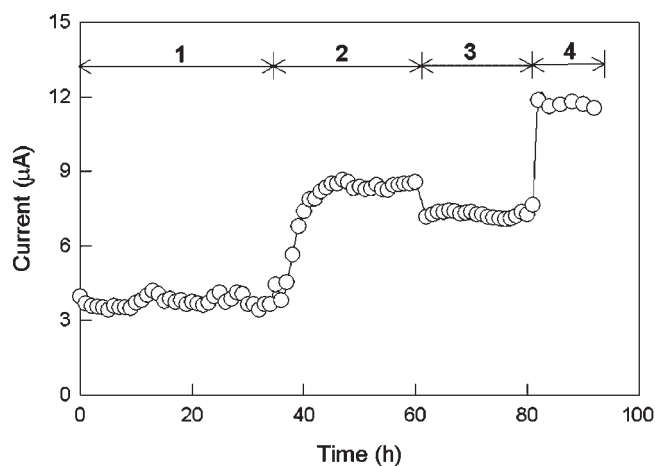


Figure 1. Current generation coupled to the oxidation of NTA with or without glucose and glutamate in oligotrophic MFCs enriched with AW containing NTA. 1, NTA was fed as the sole organic fuel at the concentration of 14.7 mg/L. 2, Artificial wastewater containing glucose and glutamate at the concentration of 10 mg/L as COD was fed with 21.8 mg/L NTA. 3, NTA was fed as the sole organic fuel at the concentration of 30.1 mg/L. 4, NTA was fed as the sole organic fuel at the concentration of 48.5 mg/L.

compound. However, NTA as a fuel is not as good as glucose/glutamate or acetate even for a copiotrophic MFC adapted with the compound. A similar trend was observed in the activated sludge processes (Bouvang and Davisson, 1972; Margarete and Thomas, 2001).

Aminobacter aminovorans, a α -proteobacterium, is known to degrade NTA under both oxic and anoxic conditions (Auling et al., 1993; Thomas, 2001). In the previous study, a high population of α -proteobacteria was detected in oligotrophic MFCs enriched with AW containing NTA (Phung et al., 2004). The efficient NTA degradation in these MFCs might be due to a high population of NTA degrading α -proteobacteria. However, α -proteobacteria related to the utilization of NTA were not found in the copiotrophic MFCs (Lee et al., 2003). It may be possible that NTA-utilizing *A. aminovorans* is an oligotroph and that other organisms are copiotrophic and degrade NTA in the MFCs where the conditions are not suitable for oligotrophs. No α -proteobacteria was found in the oligotrophic MFCs fed with river water (Phung et al., 2004).

Another possibility is that a higher redox potential is favorable for the growth of NTA-degrading α -proteobacteria in the oligotrophic MFCs. It was shown that a considerable amount of oxygen diffused into the anode compartment

through the cation-specific membrane, raising the redox potential of the oligotrophic anode compartments (Pham et al., 2004).

Since it is not known if the NTA degrading *A. aminovorans* is electrochemically active, it is most probable that this bacterium metabolizes NTA to acetate that is completely oxidized by electrochemically active bacteria in the MFC.

Use of NTA as Fuel in MFCs

Oligotrophic MFCs enriched with AW containing NTA were fed with fuel containing different concentrations of NTA, with or without glucose and glutamate, and the current was recorded (Fig. 1). The MFCs generated current with concomitant NTA removal when fed with the AW containing NTA as the sole organic compound. Higher NTA concentrations yielded higher current. These results clearly show that NTA can serve as a fuel in the MFCs.

CONCLUSIONS

In this study it was shown that NTA could be almost completely degraded in an oligotrophic MFC enriched with NTA, but not in a copiotrophic MFC. In a plug flow reactor fed with a high strength wastewater, the concentration near the outlet may be too low for the oligotrophic organisms to grow. Plug flow MFCs may be employed to remove NTA and generate a current from high strength wastewater by compartmentalizing the system. The bottom part of the MFC should be kept copiotrophic to remove the common organic contaminants and the upper part should be kept oligotrophic for oxidation of NTA.

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